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Entering Flatland in One Piece: Growth and Electronic Transport Measurements of Single Crystal Two-Dimensional Conductive MOFs

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First Reactions

Entering Flatland in One Piece: Growth and Electronic Transport Measurements of Single Crystal Two-Dimensional Conductive MOFs

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Conductive two-dimensional (2D) materials are exciting candidates for lightweight, efficient, and highly tunable technologies and often exhibit exotic electronic properties not observed in three-dimensional bulk analogues. Two-dimensional π-conjugated metal−organic frameworks (2D πMOFs) have recently joined the ever-growing 2D materials library; however, growing 2D πMOF crystals that are both amenable to device fabrication and devoid of defects and grain boundaries, which limit electrical conductivity, has proven challenging. In this issue of *ACS Central Science*,[1] Baldo, Dincă, and co-workers report a new biphasic solution−solid method for growing 2D πMOFs, producing micron-scale single crystals that can be analyzed with common electrical characterization techniques.

Two-dimensional π-conjugated metal−organic frameworks (2D πMOFs) have recently joined the ever-growing 2D materials library; however, growing 2D πMOF crystals that are both amenable to device fabrication and devoid of defects and grain boundaries, which limit electrical conductivity, has proven challenging.

In a previous study, Dincă and co-workers successfully grew single crystal rods of 2D metallic πMOFs,[2] allowing measurement of intrinsic conductivity along the *c*-axis, where organic ligands participate in interlayer $\pi-\pi$ interactions. Now, Baldo, Dincă, and co-workers turn their attention to the basal (*ab*) plane instead, where extended in-plane π−d conjugation dominates charge transport, and conductivity is expected to be higher. The authors find that two key factors can promote crystal growth in the basal plane. First, a high concentration of the organic ligand must be prealigned in a film and remain mostly solid during reaction. Second, the reaction must be confined to a very small volume.

The team demonstrates their new solution−solid method for the growth of a model 2D πMOF system, Ni-CAT-1, using hexahydroxytriphenylene (HHTP) and nickel(II) acetate ($Ni(OAc)_2$) precursors (Figure 1a). The planar HHTP ligand is thermally evaporated onto a silicon substrate, where it deposits as a thin film, and the $Ni(OAc)_2$ is coated on a second silicon substrate. The two halves are then held together by permanent magnets and immersed in solution forming a tightly bound sandwich with a very thin space in the middle where the reaction occurs. Maintaining the HHTP as a horizontally aligned solid film during reaction increases the rate of the formation of metal−ligand bonds in the basal plane, and the magnetic assembly limits growth along the *c*-axis. This method ultimately yields beautiful platelike structures that are large enough for multiterminal device fabrication—confirmed by scanning electron microscopy, Fourier-transform infrared spectroscopy, and transmission electron microscopy.

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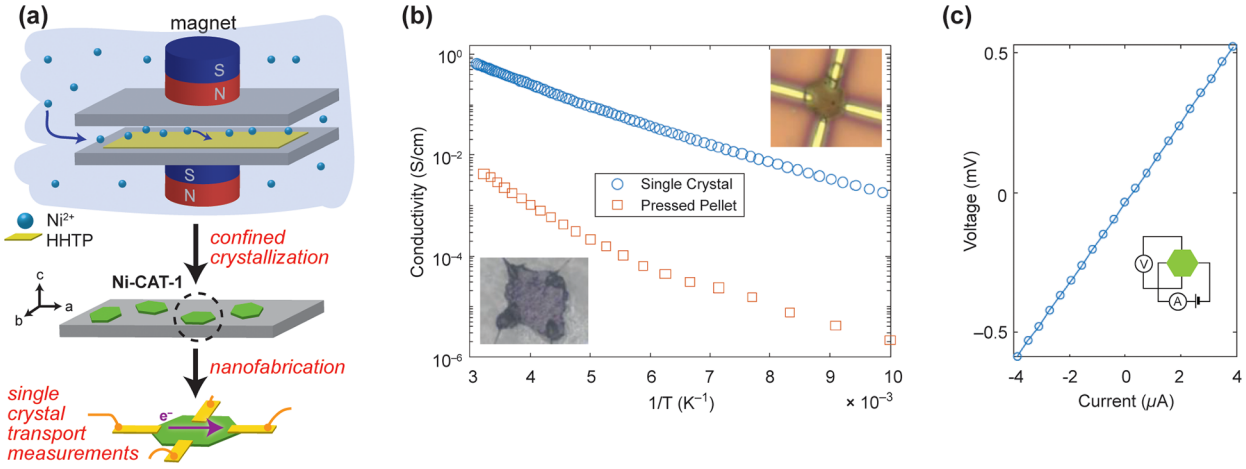

Figure 1. (a) Schematic of biphasic solution−solid growth of Ni-CAT-1 single crystals. (b) Four-probe temperature-dependent conductivity of a single crystal device (blue circles) and a polycrystalline pressed pellet device (orange squares). (c) Hall effect measurement with application of a 1 T out-of-plane magnetic field. Reproduced from ref 1. Copyright 2020 American Chemical Society.

Using a four-probe electrical measurement setup, the authors observe that Ni-CAT-1 is a semiconductor with a basal plane electrical conductivity of 2 S/cm. Remarkably, the conductivity of these single crystals grown with the solution−solid method is more than 2 orders of magnitude higher than that of the polycrystalline pressed pellet Ni-CAT-1 devices used for comparison (Figure 1b). It has been well established that trap states, which impede charge transport, often exist in grain boundaries,[3] so the observation that conductivity is higher in the single crystal samples is not surprising. However, the magnitude of the difference in conductivity between the samples demonstrates the critical importance of single crystal device measurements for deconvoluting the contributions of defects developed during synthesis from intrinsic charge transport properties.

The authors also perform Hall effect measurements on the single crystal devices (Figure 1c). In 1879, Edwin Hall discovered that an out-of-plane magnetic field exerts a force on charge carriers flowing through a material, causing an in-plane voltage to build up across the device, transverse to the direction of current flow.[4] By measuring this voltage, one can directly extract information about the charge carrier type (electrons vs holes), carrier density, and carrier mobility of a material. The Hall effect measurement is one of the most commonly employed techniques for studying the physics of 2D materials, but successful measurement does require a multiterminal device with relatively high carrier mobility.[5] While many samples, including polycrystalline and amorphous materials, can therefore be quite challenging to analyze with this technique,[6] a clear Hall effect was observed in the Ni-CAT-1 single crystals grown in this work, revealing a carrier density of 1.4×10^{19} cm^{-3}, with electrons serving as the dominant carrier type.

The solution−solid growth method designed by Baldo, Dincă, and co-workers paves the way for exploring the electronic properties and other physics in 2D πMOFs. Many questions still remain regarding the exact conduction mechanisms in these materials as well as relative contributions of in-plane and out-of-plane charge transport.[7] Due to the presence of delocalized π electrons, members of this class of MOFs have also been predicted to exhibit phenomena including topological insulator behavior,[8] the quantum anomalous Hall effect,[8] and high-temperature ferromagnetism.[9] Although a plethora of exotic physical properties have already been observed in other 2D conductive materials, including graphene, transition metal dichalcogenides, oxides, and more,[10] MOFs are unique in the exceptional tunability of their structure; since MOFs have modular structures, the organic building blocks can be modified in addition to the metal ion centers, thereby vastly expanding the landscape for synthetic design of interesting physical properties. While in this case the authors only demonstrate the growth of 2D πMOFs with different metal centers (Ni^{2+} and Co^{2+}), most organic ligands used in 2D πMOF synthesis are planar like HHTP and could likely be similarly aligned in films, in principle making the biphasic solution−solid method widely applicable. The ability to now directly probe intrinsic electronic transport along all crystallographic directions in single crystal 2D πMOFs will lend itself not only to answering existing fundamental questions about electrical conductivity in these materials, but also to guiding future synthetic efforts and continually advancing the properties of conductive MOFs for new technologies.

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Although a plethora of exotic physical properties have already been observed in other 2D conductive materials, including graphene, transition metal dichalcogenides, oxides, and more, MOFs are unique in the exceptional tunability of their structure.

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